2020-09-01

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10.1016/j.scitotenv.2020.138802
Science of The Total Environment
Elsevier BV

Mobilisation kinetics of Br, Cd, Cr, Hg, Pb and Sb in microplastics exposed to simulated, dietary-adapted digestive conditions of seabirds

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Accepted 17 April 2020
https://doi.org/10.1016/j.scitotenv.2020.138802

Abstract

Samples of beached plastics and historical and contemporary consumer plastics containing hazardous elements derived from reaction residues or functional additives have been micronised and subject to extraction conditions representative of the digestive environment of seabirds. Mobilisation of Br, Cd, Cr, Hg, Pb and Sb into NaCl solution, an avian physiologically-based extraction test (PBET) and a dietary-adapted PBET (DA-PBET) incorporating fish oil as part of the avian diet was monitored by ICP-MS over a 168-h period. Kinetic data were subsequently fitted using pseudo-first-order and parabolic diffusion models in order to derive rate constants for the release of hazardous elements during avian digestion of microplastics. Rate constants were variable and dependent on the nature and origin of plastic, type of residue or additive, extractant solution employed and model applied. Resulting estimates of bioaccessibility, defined as the equilibrium or maximum concentration of an element mobilised over the time course relative to its total concentration, were variable but considerable in many cases. Specifically, maximum values of about 65% of Cd and 100% of Pb were observed in consumer polycarbonate-acrylonitrile butadiene styrene exposed to the avian PBET and beached polyurethane exposed to the DA-PBET, respectively. The potential health risks of hazardous elements in microplastics are addressed and criteria for classification based on the European Toy Safety Directive migration (mobilisation) limits are proposed.

Keywords: microplastics; additives; metals; mobilisation kinetics; avian PBET; bioaccessibility

1. Introduction

Although the sources, distribution and physical impacts of microplastic litter have received considerable attention over the past few decades (Ng et al., 2006; Hall et al., 2015; Lin et al., 2016), less well studied are the nature, occurrence, mobility and fate of chemical residues and additives (Kwon et al., 2017; Luo et al., 2019). Residues may remain as reactants or catalysts from the manufacturing process of certain plastics or may be more widely distributed amongst plastics through the recycling and blending of end-of-use materials (Turner, 2018a). Additives are deliberately formulated into plastics, either physically or chemically, for specific functions that include flame retardancy, colour, fastness, opacity, lubrication, strength, heat resistance and stabilisation (Pritchard, 1997). While most contemporary additives are regarded as safe, many historical additives are now restricted or inhibited on health and environmental grounds. For example, the Restriction of Hazardous Substances (RoHS) Directive provides limit values of Cd, Cr(VI), Hg, Pb and certain brominated flame retardants in new or recycled electrical and electronic plastics (European Parliament and Council, 2003; 2011), while the Toy Safety Directive specifies migration limits for various metals and metalloids, including Cd, Cr(VI), Hg, Pb and Sb, from plastic toys into a fluid mimicking a child's stomach (European Parliament and Council of the EU, 2009). Despite these restrictions, however, potentially harmful residues and additives remain in products in circulation and are particularly common in marine litter where a heterogeneous assortment of plastics of variable sources and ages are encountered (Massos and Turner, 2017; Shaw and Turner, 2019).

While most residues and additives are either designed, or at least considered, to remain in the polymeric matrix, aging and weathering in the environment facilitates

their gradual mobilisation (Hansen et al., 2013; Nakashami et al., 2016). Significant in this respect is the propensity of hazardous additives, such as those listed in the RoHS, to be released into the digestive tract of animals that inadvertently or incidentally ingest plastics because mobilisation may result in their entry into the systemic circulation and subsequent accumulation. The release of small but significant quantities of Cd and Sb (typically < 1% of corresponding total values) from various micronised plastics into near-neutral surfactant- and protein-rich fluids simulating the digestive conditions of deposit-feeding invertebrates over a six-hour time period has recently been demonstrated by Martin and Turner (2019) and James and Turner (2020). In an earlier study, Turner (2018b) showed greater release (ranging from < 1% to > 20%) of various hazardous elements from polyolefins, polyvinyl chloride and expanded plastics over a more extended timeframe into an acidic solution that mimics the digestive chemistry of a seabird. Using a similar approach Tanaka et al. (2015) demonstrated mobilisation of trace quantities of the polybrominated diphenyl ether flame retardant, deca-BDE, impregnated in polyethylene. However, mobilisation was increased 50-fold when oils that simulate the presence of food were added to the acidified extractant.

In the present study, we hypothesize that the mobilisation of a variety of hazardous elements present in a wider variety of weathered and unweathered plastics are impacted by the presence of relatively hydrophobic dietary components in the avian digestive environment. Accordingly, we compare the kinetics of element mobilisation from micronised plastics (microplastics) in a standard physiologically-based extraction test (PBET) with those in a dietary-adapted-PBET (DA-PBET) in which fish oil is added. In the absence of any guidelines or limit values for environmental

plastics, measures of bioaccessibility arising from the experiments are related to available migration limits as defined by the Toy Safety Directive in order to evaluate the potential health implications of the different samples.

2. Materials and methods

2.1. Microplastic sample characteristics and preparation

Nine samples of plastic that had been archived from previous studies (e.g. Turner, 2018c; Turner and Solman, 2016) were selected for the present experiments. The origin and characteristics of the samples, shown in Table 1, indicate five different types of polymer, and five primary or secondary beached plastics that have been exposed to the environment and four historical or contemporary consumer plastics that have not undergone such exposure. Also shown in Table 1 are the concentrations of elements that are hazardous according to the RoHS Directive and determined by X-ray fluorescence spectrometry; namely, Br (a proxy for brominated flame retardants), Cr (as an upper bound indicator of Cr(VI)), Cd, Hg, and Pb. Although Sb is not in the current iteration of the RoHS, it is also included because it is used as a flame retardant synergist with brominated compounds (note its association with Br) and is regulated by the Toy Safety Directive. Significantly, all samples are non-compliant or potentially non-compliant (depending on the form of Br and speciation of Cr) with respect to the 1000 $\mu g\ kg^{-1}$ or 100 $\mu g\ kg^{-1}$ (Cd only) limit values specified by the RoHS Directive (European Parliament and Council, 2011).

About 1 g of each plastic sample was formulated to “microplastic” of less than 1 mm in at least two dimensions using a stainless steel grater. Microplastics were stored in

individual polyethylene specimen bags and in the dark pending use in the experiments.

Table 1: Characteristics of the microplastics used in the study. Polymer types were identified by Fourier-Transform infrared spectrometry and elemental concentrations (in μg g^{-1} and where nd = not detected) were determined by X-ray fluorescence spectrometry according to methods outlined elsewhere (Massos and Turner, 2017).

sample	type	description	Br	Cd	Cr	Hg	Pb	Sb
1	polypropylene	boot stud remover - black	nd	766	1180	nd	9160	109
2	polyethylene	child's shape sorter toy - yellow	nd	6880	26.0	nd	nd	nd
3	polyvinyl chloride	washing machine drainage hose - grey	73.7	nd	nd	nd	22,900	nd
4	polycarbonate + acrylonitrile butadiene styrene	jewellery beads - black, painted red	15,100	34.3	nd	nd	123	8960
5	polyethylene	water treatment medium (beached) - black	3320	nd	nd	nd	22.4	1970
6	glass-reinforced polyurethane	foam fragment (beached) - brown	50.2	nd	116	nd	4860	nd
7	polyethylene	unidentified fragment (beached) - green	1260	35.9	4970	nd	121	674
8	polyethylene	shot gun cartridge (beached) - red	6.3	1780	nd	nd	nd	nd
9	polyethylene	unidentified fragment (beached) - red	nd	969	85.5	480	21.9	nd

2.2 Extraction reagents

Extractions consisted of a 0.1 M solution of NaCl, a simulated avian physiologically-based extraction test (PBET) and a dietary adapted PBET (DA-PBET). Sodium chloride solution, simulating the pre-digestive conditions in the oesophagus and crop of seabirds, was prepared by dissolving 5.844 g of Aristar NaCl (VWR Chemicals BDH) in 1 L of high purity Elga LabWater (18.2 MΩ.cm resistivity). The standard avian PBET was based on methods outlined elsewhere (Turner, 2018b) and modelled on the chemistry of the proventriculus-gizzard of the northern fulmar, *Fulmarus glacialis*, a procelliform known to ingest substantial quantities of microplastics (Avery-Gomm et al., 2012) and an indicator species of plastic pollution according to the Oslo and Paris Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR, 2008). Here, 10 g of pepsin (lyophilised powder from porcine gastric mucosa; Sigma-Aldrich) were dissolved in 1 L of 0.1 M NaCl solution whose pH was adjusted to 2.5 by the dropwise addition of 1 M HCl (prepared from

Fisher Scientific TraceMetal grade concentrated HCl). The DA-PBET was designed to simulate digestive conditions that, additionally, include oils arising from the diet. We used oil from menhaden, fish of the genera *Brevoortia* and *Ethmidium* that are consumed by a diverse range of predators and that represent an important food source for many marine birds (Buchheister et al., 2017). Standard refined menhaden oil, comprising ~ 20-35 % omega-3 fatty acids as triglycerides and of density 0.93 g ml^{-1}, was purchased from Sigma-Aldrich.

2.3. Extraction procedure

Extractions were performed on 100 mg of each micronised sample in a series of screw-capped polypropylene centrifuge tubes using 50 ml NaCl solution, 50 ml PBET solution, and 40 ml PBET solution plus 10 ml menhaden oil (DA-PBET). The contents of the tubes were incubated under continuous lateral agitation in a water bath (Clifton, Nickel Electro Ltd, Weston-super-Mare, UK) set at 100 rpm and 40 °C. At time intervals of approximately 0.5, 1, 3, 6, 24, 48, 96 and 168 h, 4 ml aliquots of NaCl or PBET solution were pipetted from each tube, taking care not to abstract any oil from the DAPBET, and filtered through 0.45 μm Whatman membrane filters (Sigma-Aldrich) with the aid of a Terumo syringe. Filtrates were transferred to individual Sterilin tubes to which 80 μl aliquots of 2% HNO_3 (prepared from Fisher Scientific TraceMetal grade concentrated HNO_3) were added before the contents were stored at room temperature and in the dark. Controls were performed likewise for each extractant but in the absence of micronised microplastics.

In some acidified extracts from the PBET and DA-PBET a precipitate was observed to form on storage. Here, extracts were centrifuged at 3000 rpm for 10 min using an

MSE Super Minor centrifuge (Heathfeld, UK), with 1 ml aliquots of supernatant subsequently diluted to 4 ml 2% HNO_3 in new Sterilin tubes.

2.4. Extract analysis

Sample extracts were analysed in triplicate for Br, Cd, Cr, Hg, Pb and Sb by collision-cell inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermo Scientific iCAP RQ ICP-MS (Thermo Elemental, Winsford, UK) with a concentric glass nebuliser and conical spray chamber. Radio frequency power was 1550 W and coolant, auxiliary, nebuliser and collision cell gas flow rates were set at 14 L Ar min^{-1}, 0.8 L Ar min^{-1}, 1.05 L Ar min^{-1} and 5 ml He min^{-1}, respectively. Extracts were analysed in triplicate, and data were obtained over a dwell time of 10 ms with 50 sweeps per reading. The instrument was calibrated using four mixed standards (in the range 2 to 20 µg L^{-1}) and one blank prepared from LabKings and SCP Science standard solutions in 0.1 M NaCl. For quality assurance purposes, a certified reference drinking water (EP-L, SCP Science) was analysed in triplicate during each session and a standard was analysed after every ten samples as a check for instrumental drift. Limits of detection after normalisation to dry mass of microplastic ranged from about 0.003 µg g^{-1} for Cd, Cr and Pb in the DA-PBET to 0.44 µg g^{-1} for Br in NaCl solution and precision (as relative standard deviation) among replicate analyses was usually between 3 and 10%.

2.5. Timed data fitting

Data arising from the timed experiments were fitted with two diffusion models that are based on those outlined by Ruby et al. (1992). The linearised solution to the first model is as follows:

$$\ln(C_e - C) = \ln C_e - k_1 t + \ln C_0 \quad (1a)$$

where C and C_e represent the elemental concentrations mobilised from the microplastic on a weight basis at time t and at equilibrium, respectively, k_1 is a combined, forward and reverse pseudo-first-order rate constant of units h^{-1}, and C_0 is the weight-normalised concentration mobilised at $t = 0$. The latter is effectively a constant that accounts for the very rapid, initial mobilisation that is often observed to occur in such experiments but that cannot otherwise be modelled by a standard diffusion-controlled reaction (Turner, 2018b). The value of k_1 was obtained from the gradient arising from linear regression analysis of $\ln(C_e - C)$ - $\ln C_e$ versus t, using Microsoft Excel Office 365, with the value of C_0 derived from the intercept of the linear regression, a, as follows:

$$C_0 = C_e (1 - e^a) \quad (1b)$$

The linearised solution to the second, parabolic model of mobilisation is as follows:

$$C = k_2 t^{1/2} + C_0 \quad (2)$$

where k_2 is a parabolic diffusion rate constant of units $\mu g\ [g(h)^{1/2}]^{-1}$ and, as above, C_0 is the weight-normalised concentration mobilised at $t = 0$. Values of k_2 and C_0 were obtained directly from the gradient and intercept, respectively, arising from linear regression analysis of C versus $t^{1/2}$ using Microsoft Excel.

3. Results and Discussion

3.1. Elemental mobilisation among the different microplastics and extractants

The concentrations of potentially hazardous elements detected in the microplastic extracts on a mass basis and corrected for corresponding control concentrations, *C* (in $\mu g\ g^{-1}$), are shown as a function of time in Figures 1 to 6. Note that analytical error bars were often smaller than the symbol size and are not shown for clarity. There is a net increase in concentration for all elements (where detected) and all extractants over the time course, and in most cases concentrations either increase continuously over time or exhibit an initial, rapid increase followed by an approach to apparent equilibrium. For a given element, however, differences in the precise timed profiles are evident among the different samples and between the different extractant solutions.

Mobilisation of Br (Figure 1) was detected in the three microplastics where the element appeared to have been added (or recycled) as a constituent of a brominated flame retardant. Amongst the extractants, mobilisation was greatest in the DA-PBET for polyethylene (samples 5 and 7) but greatest in NaCl solution (i.e. without acidification or digestive additives) for the mixed polycarbonate-acrylonitrile butadiene styrene (sample 4). Cadmium mobilisation (Figure 2) was detected in two microplastics (samples 2 and 8) where the metal had been added as the pigment cadmium sulphide yellow, CdS, or cadmium sulphoselenide red, Cd_2SeS (confirmed from the sample X-ray fluoresence spectra), and in two microplastics (samples 1 and 4) where it was present as a contaminant (likely through recycling); significantly, Cd release was not detected in polyethylene (sample 9) where the metal had been added

261 with Hg (presumably as the pigment cadmium mercury red, $CdHgS_2$), although
262 measureable mobilisation of Hg itself by the DA-PBET was evident (Figure 4).
263 Cadmium mobilisation was always greater in the PBET and DA-PBET than in NaCl
264 solution, with maximum release effected by the PBET and the DA-PBET in two cases
265 each. Chromium mobilisation (Figure 3) was detected from polypropylene (sample 1)
266 and polyurethane (sample 6) where the metal was likely present as a contaminant or
267 residual catalyst but not in polyethylene (sample 7) where it was present at the highest
268 total concentration as a pigment (and most likely chromium oxide green; Cr_2O_3). In
269 both cases of detectable Cr mobilisation, the DA-PBET released considerably greater
270 quantities of the metal than the PBET and NaCl solution.
271
272 Lead mobilisation was detected in four cases (Figure 5); in polypropylene (sample 1)
273 and polycarbonate-acrylonitrile butadiene styrene (sample 4), where the metal was
274 likely present as a contaminant, release was greatest by the PBET, while for polyvinyl
275 chloride (sample 3) and polyurethane (sample 6), where the metal was likely present
276 as part of a stabilising compound or catalytic residue, respectively, release was
277 greatest for the DA-PBET. Mobilisation of Sb (Figure 6) was detected in the
278 microplastics where it was co-associated with Br (samples 4, 5 and 7) and in the
279 microplastic where it was likely present as a contaminant through recycling (sample
280 1). Mobilisation was greatest for the DA-PBET in all cases with the exception of
281 sample 4; here, the PBET mobilised the greatest quantity of the metalloid and the DA-
282 PBET mobilised the lowest concentration.
283
284 *3.2. Kinetic modelling of timed data*

285 Rate constants and values of C_0 derived from the timed mobilisation data shown in
286 Figures 1-6 are given in Table 2. The criterion for assigning a value of either k_1 or k_2
287 was based on the shape of the timed profile (approach to equilibrium or a more
288 continuous increase in concentration with time, respectively) and the model regression
289 fit that yielded the greater significance. Where k_1 was assigned, the value of C_e,
290 defined as the concentration measured at the termination of the experiment, is also
291 shown. Note that any concentrations exceeding this value through the time course
292 were neglected in the derivation of the rate constant (i.e. $n < 7$ in the regression).
293 Where k_2 was assigned (and denoted with an asterisk in Table 2), the final
294 concentration measured in the time course is given but here is defined as the
295 maximum concentration, C_{max} (and $n = 8$ in the regression). Where neither model
296 returned a significant fit but mobilisation was detected, C_{max} is shown.

297

298 **Table 2:** Constants defining the timed data show in Figures 1 to 6 for elemental
299 mobilisation from 9 samples of microplastics in NaCl solution, the PBET and the DA-
300 PBET. Note that ns = not significant, and values highlighted in yellow or orange
301 denote, respectively, non-compliance or potential non-compliance with respect to the
302 European Toy Safety Directive (European Parliament and Council of the EU, 2009).

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Cd		Cr			Hg	Pb			Sb		
PBET	DA-PBET	NaCl	PBET	DA-PBET	DA-PBET	NaCl	PBET	DA-PBET	NaCl	PBET	DA-PBET
400*	0.857*	0.0140	0.0094	0.0487		0.0201	0.0141	0.0116	0.0160	0.0138	0.0283
.26*	10.8*	11.4	13.9	25.9		230	445	295	1.70	4.10	9.90
0.500	-0.237	5.58	7.32	5.92		98.2	204	37.5	0.098	0.578	0.126
957 (8)	0.970 (8)	0.746 (7)	0.771 (7)	0.968 (7)		0.911 (7)	0.890 (7)	0.982 (7)	0.961 (7)	0.938 (7)	0.978 (7)
.75*	5.42*										
7.0*	65.6*										
.459	1.88										
991 (8)	0.963 (8)										
						ns	0.452	0.0251			
						99.1	1150	1900			
							711	660			
							0.992 (4)	0.900 (7)			
0289	0.0193					ns	0.0199	0.0252	16.9*	34.1*	8.50*
22.2	18.4					0.60	32.5	18.0	223*	440*	112*
.890	2.31						10.9	5.97	22.9	21.5	-0.465
964 (7)	0.983 (7)						0.969 (7)	0.886 (7)	0.960 (8)	0.987 (8)	0.998 (8)
									0.785*	1.08*	0.0312
									13.0*	14.7*	35.2
									0.189	-0.675	12.0
									0.996 (8)	0.976 (8)	0.989 (7)
		0.0207	ns	0.472		0.0233	0.228	0.0224			
		0.500	1.14	6.20		2000	2700	5130			
		0.409		5.72		1340	1760	4350			
		0.675 (7)		0.844 (3)		0.793 (7)	0.985 (5)	0.691 (7)			
									0.0234	0.0147	0.0295
									6.50	7.20	15.2
									-0.917	-0.147	7.83
									0.924 (7)	0.986 (7)	0.691 (7)
804*	0.383*										
2.1*	5.34*										
0.224	0.0308										
373 (8)	0.978 (8)										
					0.140*						
					2.30*						
					0.364						
					0.949 (8)						

Rate constants arising from model 1 range from 0.0094 h^{-1} for Cr in sample 1 exposed to the PBET to 0.472 h^{-1} for Cr in sample 6 exposed to the DA-PBET. Values of C_0 were usually positive and in many cases exceeded 50% of C_e (e.g. Pb in sample 6), suggesting significant instantaneous mobilisation into the extractants. Rate constants arising from model 2 range from 0.119 μg $[g(h)^{1/2}]^{-1}$ for Cd in sample 1 exposed to NaCl solution to 34.1 μg $[g(h)^{1/2}]^{-1}$ for Sb in sample 4 exposed to the PBET, and here values of C_0 were always relatively close to the origin.

3.3. Elemental bioaccessibilities

Table 3 provides operational measures of elemental avian bioaccessibility, BA (%), or the percentage of total element that is available in the pre-digestive environment of

the oesophagus and crop (NaCl), the digestive environment of the proventriculus and gizzard in the absence of food (PBET) and the digestive environment in the presence of food (DA-PBET) over a timeframe of 168 h. (Note that non-food material may be trapped in the proventriculus-gizzard of many seabirds for weeks to months; Avery-Gomm et al., 2012.) Values of BA are calculated from the equilibrium or maximum (i.e., final) concentrations of elements mobilised over the time courses and reported in Table 2 relative to corresponding total elemental concentrations determined by X-ray fluorescence spectrometry and given in Table 1. Where an element was detected by X-ray fluorescence but not detected by an extractant an upper limit is given based on the ICP-MS detection limit in the relevant medium.

Table 3: Percentage bioaccessibilities of hazardous elements in the different extractants tested and calculated from C_e or C_{max} relative to total concentration.

	Br			Cd			Cr			Hg	Pb			Sb		
sample	NaCl	PBET	DA-PBET	NaCl	PBET	DA-PBET	NaCl	PBET	DA-PBET	DA-PBET	NaCl	PBET	DA-PBET	NaCl	PBET	DA-PBET
1				0.226	0.687	1.41	0.473	1.18	2.19		2.51	4.86	3.22	1.56	3.76	9.08
2				0.346	0.683	0.953										
3	<0.600	<0.039	<0.004								0.430	5.25	8.67			
4	4.90	0.038	0.094	16.9	64.7	53.6					0.488	26.4	14.6	2.49	4.91	1.25
5	0.274	1.33	1.61											0.660	0.746	1.8
6	<0.880	<0.058	<0.006				0.431	0.980	5.34		41	56	106			
7	0.095	0.349	2.14	<0.096	<0.014	<0.009	<0.001	<0.001	<0.001		<0.004	<0.010	<0.002	0.964	1.07	2.26
8				0.183	0.680	0.300										
9				<0.001	<0.001	<0.001	<0.004	<0.004	<0.004	0.048						

For a given element, values of BA vary considerably amongst the microplastics and extractants. For Br, BA ranges from < 1% for samples 3 and 6 in all extractants to about 5% for sample 4 exposed to NaCl. For Cd, BA is < 1 % in most cases with the exception of sample 4 where values exceed 50% in the PBET and DA-PBET; in all samples where the metal was detected in the extractants, BA was greater in the PBET

or DA-PBET than in the near-neutral NaCl solution. For Cr, BA ranges from < 0.005% in samples 7 and 9 to > 2% for samples 1 and 6 exposed to the DA-PBET. Values of BA for Pb range from < 0.01% in sample 7 to about 100% in sample 6 exposed to the DA-PBET, and in all cases BA was greater in the PBET or DA-PBET than in NaCl solution. Regarding Sb, BA ranges from 0.66% in sample 5 exposed to NaCl to over 9% for sample 1 exposed to the DA-PBET, and in all microplastics the maximum value of BA results from exposure to the PBET or DA-PBET.

3.4. Mechanisms of element mobilisation

Hazardous elements may be incorporated into the plastic as ions, complexes or compounds, or bound irreversibly to the polymeric backbone (Town et al., 2018). In addition, at least for the beached plastics, there may be a small amount of element adsorbed to the surface from the marine environment (Holmes et al., 2012). Neglecting desorption of environmentally acquired elements, the fundamental mechanism of element mobilisation from the microplastics in the present study is diffusion from the plastic matrix into a saline (NaCl) aqueous medium. Free ions and small complexes may diffuse through the particle matrix whereas larger complexes or those bound irreversibly are immobile, with the permeability (or crystallinity) of the polymer determining the size limit of diffusible complexes. Presumably, therefore, the rapid, instantaneous mobilisation that we observe arises from the release of elements that are located at (but incorporated into) the particle surface and not required to diffuse through the plastic matrix.

The rate of mobilisation of elements from the microplastics may be facilitated by altering the composition of the aqueous medium, or, more specifically, making

conditions more favourable for the formation of free ions or small complexes and molecules. To this end, the use of an acidic digestive medium is predicted to increase the concentration of metal ions relative to a near-neutral solution. Mobilisation may also be facilitated if a medium is introduced that interacts with the plastic matrix by, for example, exposing a greater surface area to the aqueous phase through polymer chain loosening (Sun et al., 2019). Accordingly, it is possible that the hydrophobic fish oil is able to partially modify the integrity of plastic structure or even act as a solvent for the extraction of relatively hydrophobic organic compounds of bromine (Tanaka et al., 2015).

The observations in the present study are partly consistent with the assertions above in that mobilisation and bioaccessibility of the metals (Cd, Cr and Pb) are enhanced under the acidic conditions of the PBET and DA-PBET relative to unacidified NaCl solution, with the presence of fish oil usually enhancing but sometimes inhibiting metal release. Acidified conditions also promote the mobilisation of Br and Sb in most cases, but NaCl releases greater quantities of both elements than the PBET and/or the DA-PBET from sample 4. The polymeric composition of this sample (acrylonitrile butadiene styrene-polycarbonate) suggests a rather amorphous structure of relatively low permeability and high thermal stability, at least compared with expanded polyurethane, polyvinyl chloride and the polyolefins (Keller, 2017). Anomalous mobilisation results for sample 4 in the presence of fish oil (for Br and Sb as well as Cd and Pb) may, therefore, reflect the poor penetrability of the relatively large triglyceride molecules into the plastic and, possibly, a propensity to block the migration of other solutes into and out of the matrix.

3.5. Implications for exposure to seabirds and setting safety guidelines

Despite kinetic modelling of the mobilisation of potentially hazardous elements from microplastics under simulated digestive conditions being relatively straightforward, the extent of mobilisation exhibits a complex dependence on the type of plastic, the nature of the additive or reaction residues and the composition of the extractant solution. Mobilisation is, however, considerable in many cases, with a reduction in pH facilitating elemental release for metals and the presence of food oil having a more variable but usually positive effect on the dissolution of both inorganic and brominated compounds. For more meaningful upper estimates of chemical bioaccessibility in microplastics and their risks to fish-consuming seabirds, it is recommended that both a standard avian PBET and a DA-PBET be employed and that the higher result be adopted.

Currently, there exist no chemical standards for waste environmental plastics that are based on health grounds. The RoHS Directive limits have recently been employed as a screening criterion for compliance of primary and secondary beached plastics (Shaw and Turner, 2019) but the total content of a potentially hazardous chemical does not address its potential for migration or its bioaccessibility to an animal. Accordingly, we propose that the Toy Safety Directive limits on the migration of metals and metalloids (but not brominated compounds) are of most relevance when evaluating the potential health impacts of marine plastic ingestion to mammals. Here, limit values are based on the potential impacts arising from the ingestion of 8 mg of material per day and migration into 0.07 M HCl for 2 h at 37^{o}C (BSI, 1994; European Commission, 2016). Current or proposed migration limits for material that can be "scraped off" toys, including plastics, by biting and sucking are 17 $\mu g\ g^{-1}$ for Cd, 0.2 $\mu g\ g^{-1}$ for Cr(VI),

94 μg g^{-1} for Hg, 23 μg g^{-1} for Pb and 560 μg g^{-1} for Sb (European Parliament and Council of the EU, 2009). Based on these limits, and for an equivalent weekly (168 h) intake of 56 mg of microplastic by a seabird, five of the current samples that include beached plastics and both historical and contemporary consumer products would be non-compliant with respect to at least one element and at least one extractant; non-compliance occurs for Pb in four cases, Cd in two cases, and Cr in one case (sample 1) if it is assumed that a Pb-Cr association is indicative of lead chromate and the higher oxidation state of the metal.

Clearly, the overall risk to a seabird is more complex as plastic ingestion varies greatly between and among species (Lavers and Bond, 2016; Roman et al., 2019) and the quantities of plastic ingested that contain hazardous elements will depend on availability in the water column, foraging ecology, and any selectivity based on, for example, colour (Kain et al., 2016; Tavares et al., 2017). Nevertheless, microplastics should not be overlooked as a source of harmful additives and residues to animals that digest material for extended periods of time under acidic and oily conditions.

4. Conclusions

Significant quantities of hazardous elements (Br, Cd, Cr, Hg, Pb, Sb) associated with residues and historical additives in plastics can be mobilised under simulated gastric conditions representative of seabirds, and in particular where the diet is considered as part of the digestive chemistry. Although the kinetics of mobilisation can be modelled by simple diffusion equations, the magnitude of the constants associated with these models appear to exhibit a complex dependence on the nature of the additive and the type and condition of the plastic. It is suggested that limits of chemical migration (or

mobilisation) stipulated by the European Toy Safety Directive afford a means of evaluating the potential risks of microplastics to mammals in the marine environment. On this basis, five out of nine plastics tested in the present study returned non-compliant concentrations for at least one element and one digestive fluid simulant.

Acknowledgements

Dr Robert Clough, Dr Andrew Fisher and Mr Andy Arnold (UoP) are thanked for technical assistance and advice throughout the study. This work was supported in part by a Higher Education Innovation Fund grant.

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610 Figure 1: Mobilisation of Br from micronised plastic samples as a function of time in
611 NaCl solution (blue circles), the PBET (green triangles) and DA-PBET (orange
612 squares).
613

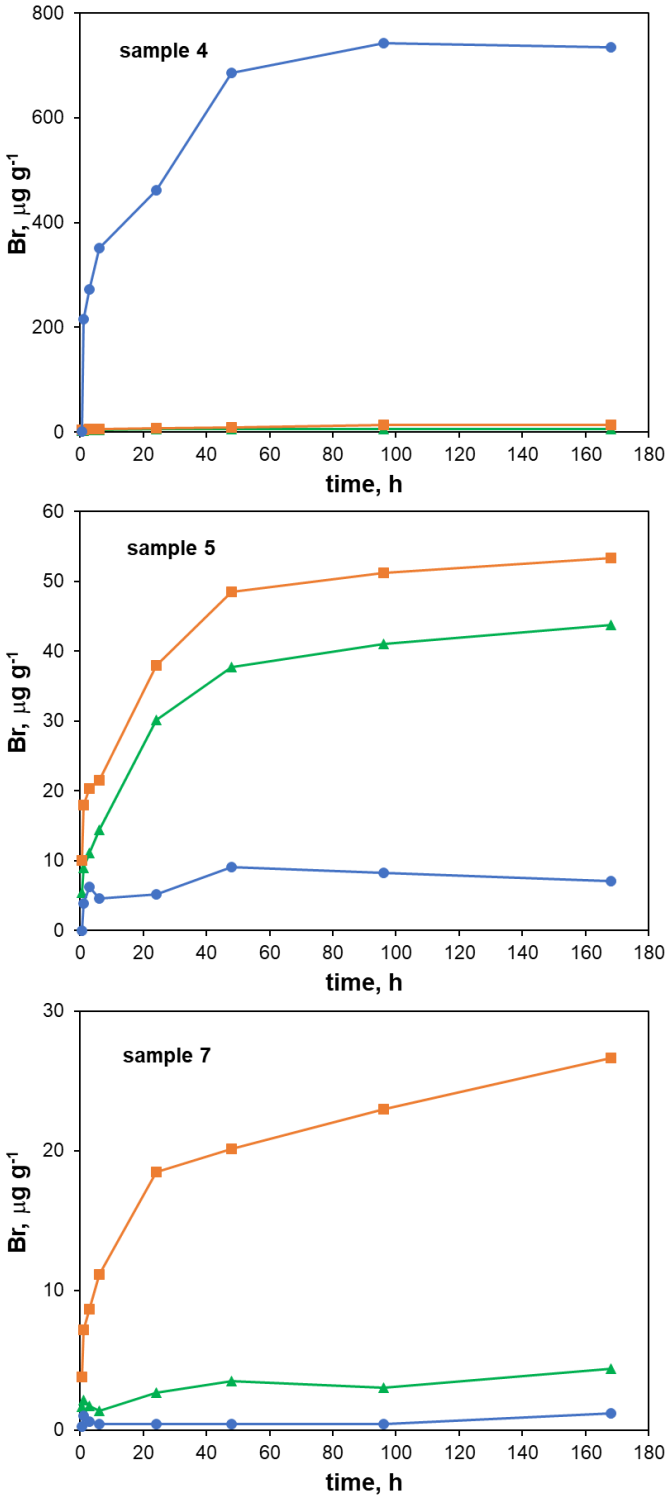

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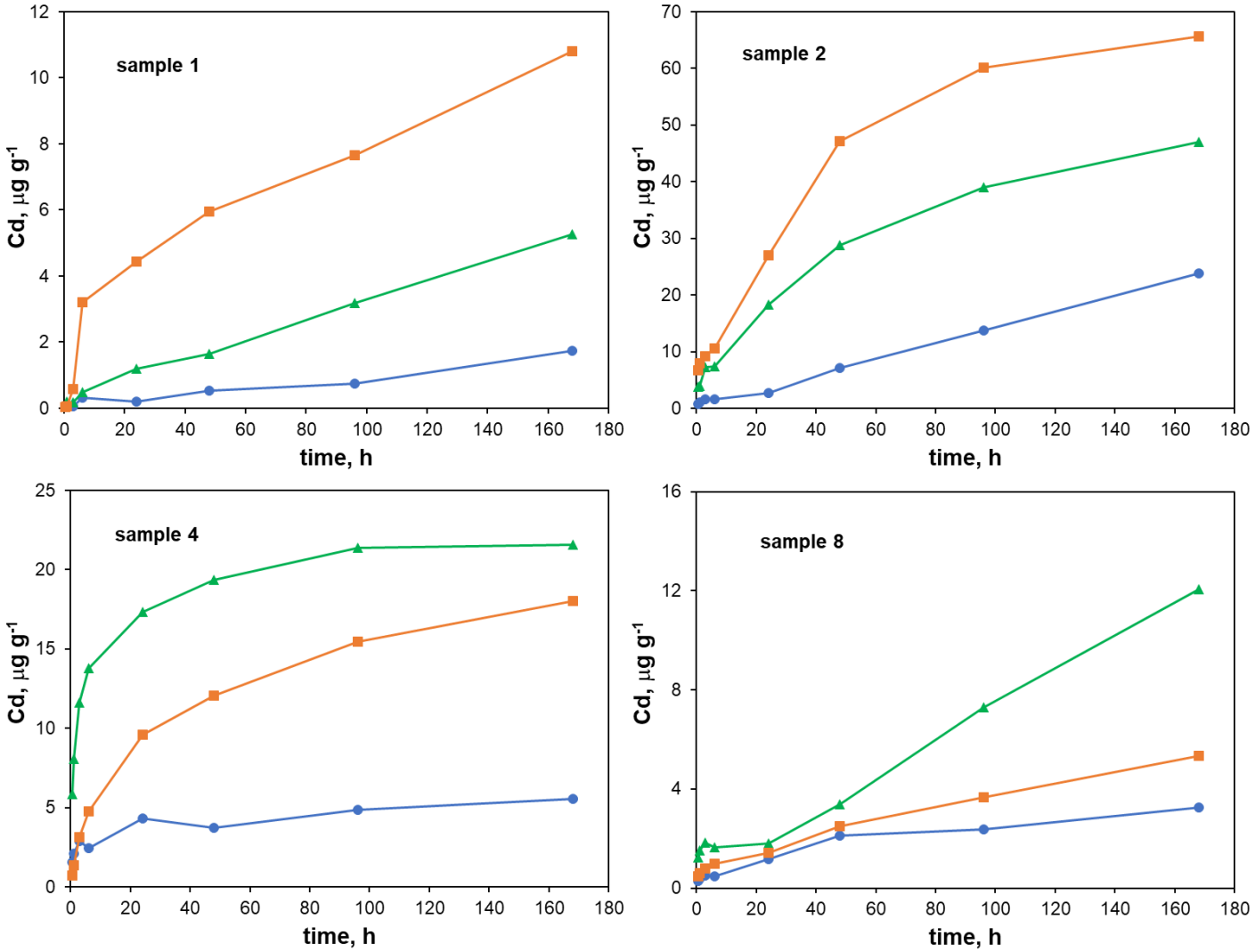
Figure 2: Mobilisation of Cd from micronised plastic samples as a function of time in NaCl solution (blue circles), the PBET (green triangles) and DA-PBET (orange squares).



618 Figure 3: Mobilisation of Cr from micronised plastic samples as a function of time in
619 NaCl solution (blue circles), the PBET (green triangles) and DA-PBET (orange
620 squares).
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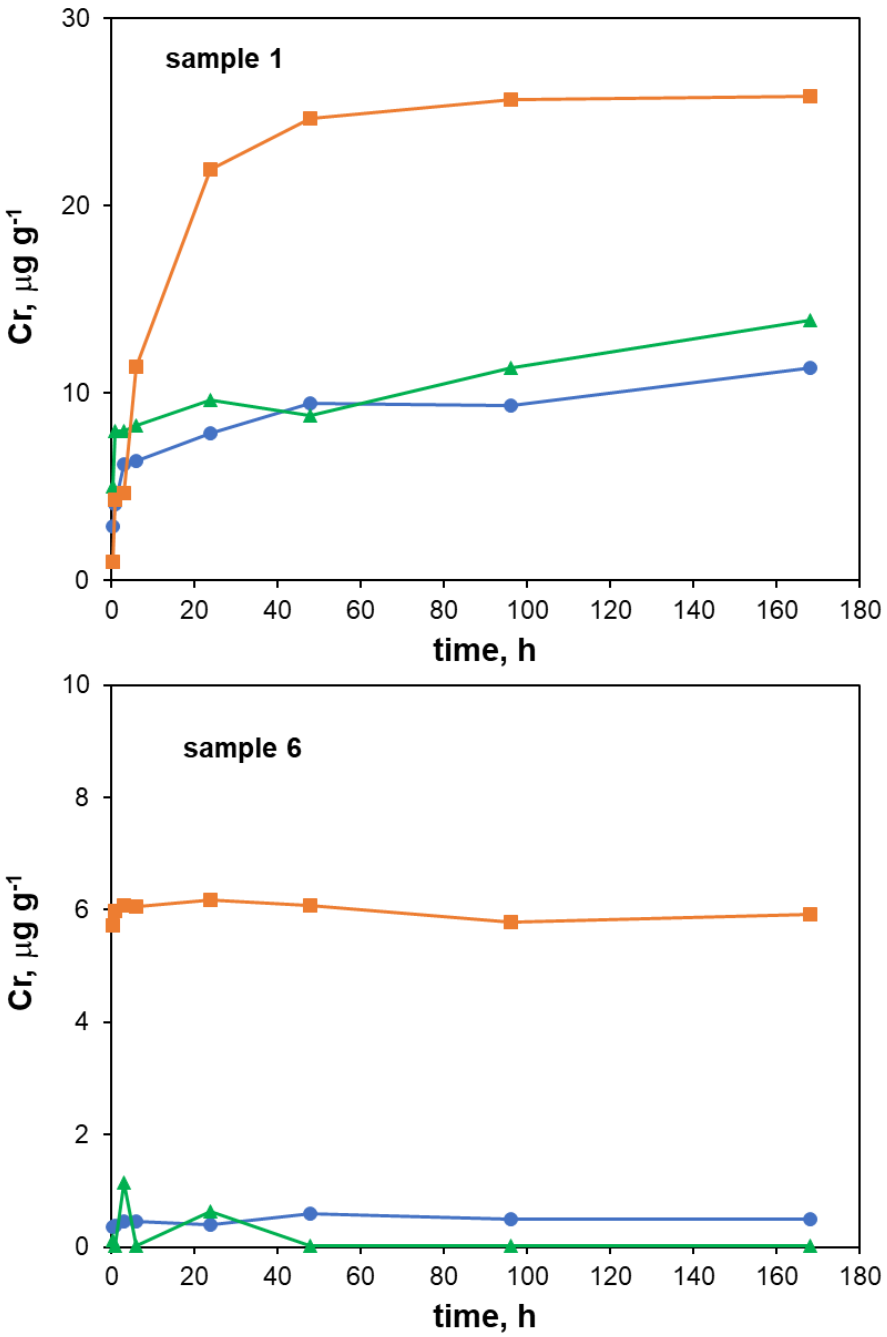
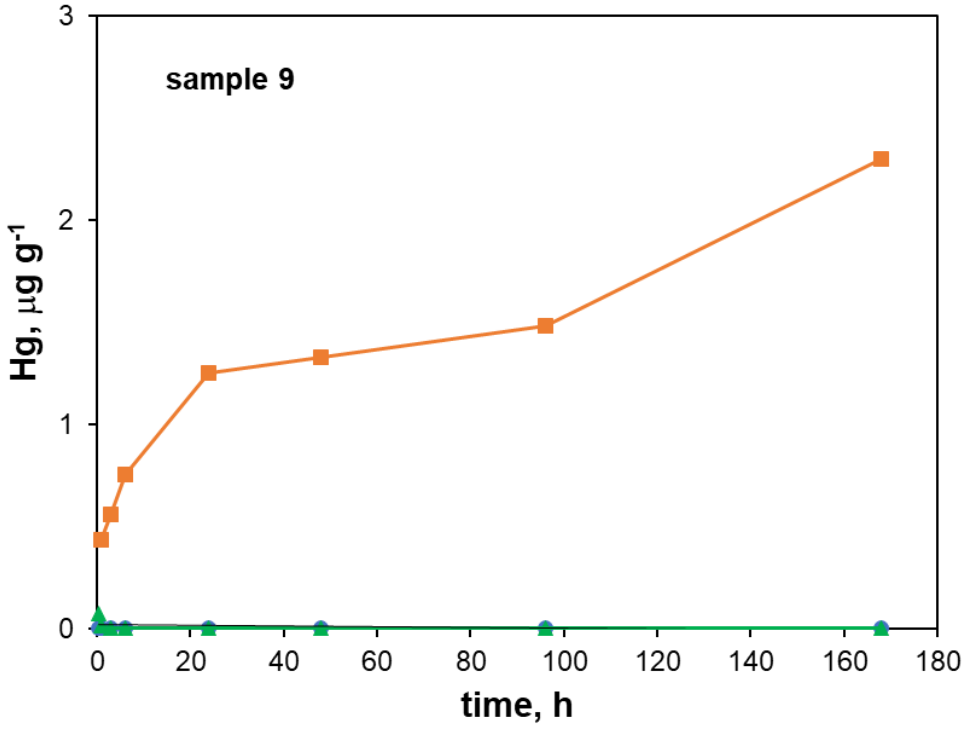


623 Figure 4: Mobilisation of Hg from a micronised plastic sample as a function of time in
624 NaCl solution (blue circles), the PBET (green triangles) and DA-PBET (orange
625 squares).



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627 Figure 5: Mobilisation of Pb from micronised plastic samples as a function of time in NaCl solution (blue circles), the PBET (green triangles)

628 and DA-PBET (orange squares).

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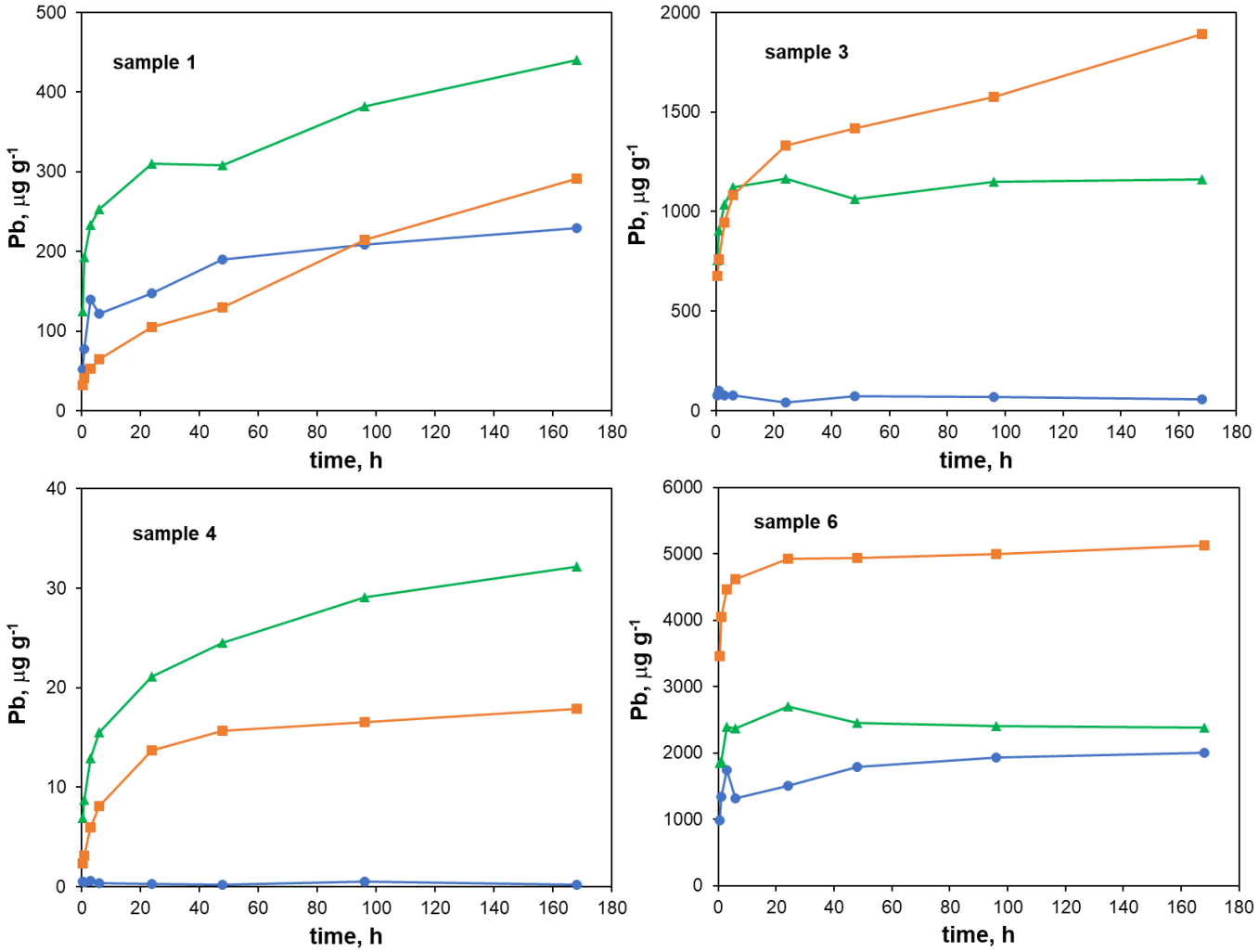

631 Figure 6: Mobilisation of Sb from micronised plastic samples as a function of time in NaCl solution (blue circles), the PBET (green triangles)

632 and DA-PBET (orange squares).

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